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Original article

Non-invasive characterisation of binding media on painted glass magic lantern plates using mid-infrared fibre-optic reflectance spectroscopy

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Abstract

Painted glass magic lantern plates from the Museo Nazionale del Cinema, Torino (Italy), were studied using mid-infrared (mid-IR) fibre-optic reflectance spectroscopy (FORS), a non-invasive technique, to test its potential for the identification of the types of binding media used in the paints. Gum, oil and resin media were identified on the plates and the amounts of these media varied from place to place; the discovery of these media correlate well with the literature on magic lantern plate preparation and painting. The spectra collected are reported uncorrected and also with the fingerprint region corrected with the Kramers–Kronig correction, which corrects distorted peaks caused by specular reflections.
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1. Introduction

Mid-IR fibre-optic reflectance spectroscopy (FORS) is a non-invasive and flexible technique which allows one to examine unique objects and materials. This technique has been used in the conservation field for about 10 years [1,2] and continues to gain popularity. The fibre-optic probe is designed to be coupled with a Fourier transform infrared (FTIR) bench unit and contains a bundle of fibres, transparent in the mid-IR spectral region, with a number dedicated to directing the radiation to the object and the others dedicated to directing the radiation reflected back from the object. In situ, mid-IR measurements on objects are possible if the fibres are coupled with a portable spectrophotometer. The analyses can be done with or without contact with the surface of the material and perpendicular or angled, as desired for optimising the collected spectrum [3].

Painted glass magic lantern plates are delicate objects, thus a non-invasive and non-destructive technique, such as mid-IR

FORS, is ideal for the characterisation of the binding media present on these plates. Described as the ancestors of the modern slides for slide projectors, the plates consisted of a carefully painted image on a clear glass surface which was held in place by wood or another type of support. The slide image was projected onto a suitable screen by a magic lantern and was an early form of entertainment and also used for scientific optical experiments [4]. The projection was done by passing a bright beam of light through the slide followed by an enlarging lens.

Though the 15th to the 19th centuries, the images on the magic lantern slides were painted by hand; these elaborate hand-painted glass slides are considered to be miniature masterpieces of their own. With the invention of photography in the 19th century, photographic plates quickly became popular, and hand painting on glass became almost a lost art [4]. Since this paper focuses on hand-painted glass plates, photographic magic lantern plates will not be discussed. The main painting techniques described in the literature involved watercolour and oil, and often both on the same piece of glass. Sometimes tempera (animal glue) was also used. In some cases, to help realise the design, a very thin layer of varnish, diluted gelatin or a solution of water and sugar was first placed on the glass. This allowed the artist to lightly draw a design on top with a thin brush and black pigments or a neutral colour, with a pencil, with chalk or with calcium carbonate. A more simple method, with lower quality

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results, was to trace a design on a sheet of gelatin using a thin point and carefully rubbing a fine powder of lead on the surface, which was deposited in the incisions. Another method frequently used, especially to obtain realistic images, was to place a clean glass over a design and copy it directly using coloured paints without creating an outline. [4].

The oil colour technique used the more transparent traditional oil colours. The paint was added in at least three layers, where the second and third layers were painted with more luminous and pure colours. Once complete, the paint surfaces were cleaned and varnished, where necessary, with a very dilute varnish. For the painted glass magic lantern plates, where fine details and clarity were essential, a fine design was first laid-out on a flat piece of glass and coloured in with watercolours over which was spread a layer of varnish to give the necessary transparency to the image. This method was established and used by the British microscopist Rev. Dr D. Dallinger in the 19th century [4].

The spectra obtained by mid-IR FORS are generally low in intensity (reflected energy is usually in the range of 1–2% [2]), noisy [2] and complicated; thus, making them difficult to interpret. Distortions in the spectra, such as shifts in absorption frequencies and changes in peak shapes are also observed in mid-IR FORS spectra making them difficult or impossible to compare with transmission and ATR spectra [2,3]. Many of these distortions originate from specular reflection; these distortions, including reststrahlen (residual energy) bands and peaks which resemble first order derivatives, must be carefully interpreted and corrected, when possible. Also surface topography and geometry have effects on the shapes of the spectra [5]. In some cases, spectral corrections can be employed to aid in the interpretation of the results. For example, with some spectral distortions caused by specular reflection the Kramers–Kronig correction can be used [1,2,6]. Also, the specular component of the reflection can be decreased by the inclination of the fibres; however, this leads to signal loss [3]. When using the Kramers–Kronig correction, special attention should be paid [6] to the algorithm in the software concerning the correction to ensure that it is valid for the case at hand.

Another important point is the possibility of interferences between adjacent thin layers, which has been observed using mid-IR FORS. Unfortunately, it is impossible to discriminate between separate layers during spectra collection and personal judgement based on other knowledge of the artwork must be used for spectra interpretation.

Mid-IR FORS can be considered a complementary technique to Raman spectroscopy. Raman spectroscopy, although having a higher signal output, resolution and less noise problems, can suffer from fluorescence from the organic materials complicating significantly spectra interpretation. In cases where fluorescence is an issue, mid-IR FORS can be a useful tool for organic binder identification.

Presented in this paper are mid-IR FORS characterisation results of the binding materials used in the painted images on two glass magic lantern plates from the Museo Nazionale del Cinema's collection in Torino, Italy. The two magic lantern glass plates studied were *Ponte del Diavolo-Giorno* and *Ponte del*

Diavolo-Notte and are described in more detail in the experimental section.

2. Experimental

Reflectance spectra were acquired using a Thermo Nicolet FTIR-NEXUS spectrophotometer, connected to a REMSPEC fibre-optic immersion probe and a liquid nitrogen cooled Mercury Cadmium Telluride (MCT) detector. The Y-shaped fibre-optic probe had a tip length of 10 mm with fibres (500 μm each in diameter) made of chalcogenide, with a glass core matrix of an As–Se–Te mixture and a As, Se, S glass cladding mixture. The probe contained a 19-fibre bundle; seven fibres sent the radiation to the sample, and the other 12 were dedicated to guiding the reflected energy to the detector. Spectra were collected from 4000 cm^{-1} to 1000 cm^{-1} with 4 cm^{-1} resolution and 128 scans. A polished piece of aluminium was used as the reference material for the background spectrum. The probe, securely mounted with a retort stand with clamps, was kept at a 90° angle to the sample surface and a small space of approximately 1 mm was left between the probe and sample surface. This distance was chosen to minimise the risk of accidental contact with the surface of the plate still having a relatively good signal. If the probe is too far from the surface, much of the signal is lost and the spectra become much lower in intensity. Data was collected and analysed in OMNIC 6.1a software. Employed in some cases to help with the interpretation of the spectra was the Kramers–Kronig correction. The spectra were all smoothed to 25 cm^{-1} . The probe set-up can be seen in Fig. 1.

Some limitations of the fibres and technique are undesired absorptions; the fibres show an Se–H stretching absorption in the 2050 to 2250 cm^{-1} range altering the signal to noise ratio in that region. Environmental moisture at 3100–3500 cm^{-1} and carbon dioxide at 2250 cm^{-1} can also cause interference, blinding the regions [1,7].

FTIR-attenuated total reflectance (ATR) spectra were collected with a Smart Endurance ATR accessory, from 4000 cm^{-1} to 500 cm^{-1} and for 32 scans and a resolution of 4 cm^{-1} .



Fig. 1. *Ponte del Diavolo-Giorno* (painted side of glass plate) and fibre-optic probe set up.



Fig. 2. Mid-infrared (IR) spectra (uncorrected) of the four reference materials. From top to bottom: linseed oil, gum arabic, rabbit skin glue and Venetian turpentine. Taken at a 90° angle to the sample surface. Arbitrary axis, smoothed by 25 cm⁻¹.

The painted glass magic lantern plates were *Ponte del Diavolo-Giorno* (The Devil's Bridge-Day) and *Ponte del Diavolo-Notte* (The Devil's Bridge-Night). Both plates were from Germany and were made in the second half of the 19th century. They were designed to be "dissolving views", both having the same scene: a bridge, house and countryside at two different moments during the day. One plate represented the scene in the daylight with the light of the sun and the other represented the scene in the twilight of the night. Placed over one another during the projection gave the effect of the transition between day and night.

Reference samples were prepared on glass microscope slides and measured the same way as the glass magic lantern plates. Thin film reference samples of clarified linseed oil (used to represent an oil paint, from Lefranc & Bourgeois, France), rabbit skin glue (bulk from Rima, a local art supplies store), gum arabic (Water Colour from Winsor & Newton, England) and Venetian turpentine (from Talens, Holland) were prepared and analysed for comparison purposes.

3. Results and discussion

The reference materials were helpful for the interpretation of the spectra collected on the painted glass magic lantern plates. Oil colours (linseed oil), watercolours (natural gums) and tempera (animal glues) were the most widely used painting materials for glass magic lantern plates, as well as varnish materials; thus, reference samples of these materials were prepared. Linseed oil (uncorrected) had a characteristic first order derivative specular distortion C=O vibration peak at 1754 cm⁻¹. Also present, were the CH₂ stretching peaks at approximately 2951 cm⁻¹ and 2850 cm⁻¹ and in the noisier fingerprint region there were peaks around 1478 cm⁻¹ and 1252 cm⁻¹. Gum arabic (uncorrected) had a very characteristic distorted C–O peak at 1170 cm⁻¹ and peaks at 1456 cm⁻¹ and 1670 cm⁻¹. Rabbit skin glue (uncorrected) had a very characteristic first order distorted peaks at

1704 cm⁻¹ from the C=O in the amide group of the protein (amide I) and 1578 cm⁻¹ from the C–N–H bending vibration of the protein (amide II). The Venetian Turpentine reference (uncorrected) had a characteristic distorted C=O peak around 1735 cm⁻¹ and fingerprint peaks at approximately 1465 cm⁻¹, 1274 cm⁻¹, 1147 cm⁻¹ and 1065 cm⁻¹. The reference spectra can be seen in Fig. 2. To help in the interpretation of the distorted spectra, the Kramers–Kronig correction was applied to the fingerprint regions, and it can be seen in Fig. 3 how successful the correction was in correcting the specular distortions in the reference spectra. Shown are the corrected fingerprint regions of each reference spectra compared to their FTIR-attenuated total reflectance (ATR) spectra respectively. In all the cases, except for part of the turpentine spectrum, the Kramers–Kronig correction worked well to correct the spectra, making them appear in a more traditional fashion. It should be noted that the mid-IR FORS spectra and FTIR-ATR spectra have different resolutions, 25 cm⁻¹ and 4 cm⁻¹ respectively. As a result, the spectra shapes and relative position of the peaks were compared, since exact peak matching is not possible.

An important observation to note is the shifting of the peaks to longer wave numbers in the FORS spectra compared to the values reported for transmission and attenuated total reflectance spectra. This is likely due to the contribution of the specular reflection [7]. Other phenomena observed were the distortions of some of the main absorbance peaks into peaks resembling first order derivatives and reststrahlen bands due to the intense reflectance maxima.

Ten areas were examined on each piece (Figs. 4a and b), with the probe at a 90° angle to the sample surface. Unfortunately, since the *Ponte del Diavolo-Notte* was so heavily damaged, the sample points between the two plates do not correspond with each other. Observed were variations of the paint binder composition from area to area; in each point the components remained the same but varied in concentration. On the *Ponte del Diavolo-Giorno* and *Notte*, the binding materials identified

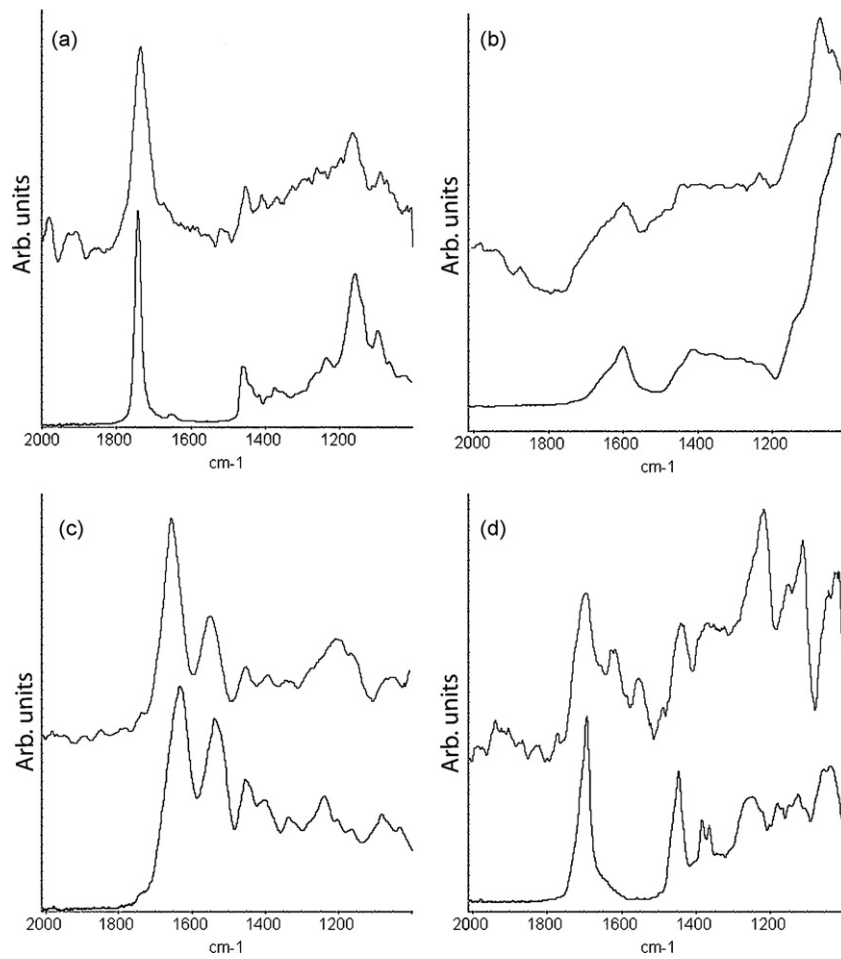


Fig. 3. The Kramers–Kronig corrected fingerprint regions (top spectra) of the reference spectra compared to the FTIR-ATR spectra (bottom spectra) of the same materials respectively: a: linseed oil; b: gum Arabic; c: rabbit skin glue and d: Venetian turpentine.

were oil, watercolour (gum arabic or a gum or sugar material with a similar infrared spectrum) and a resin. The gum material observed was likely part of a preparatory layer, since it was more prevalent in areas without much colour. Also suspected was an

oil/resin paint-binding material or a varnish layer or layers over an oil paint. In some spectra there were distortions resembling reststrahlen bands that distorted much of the fingerprint region making binder identification very difficult or impossible.

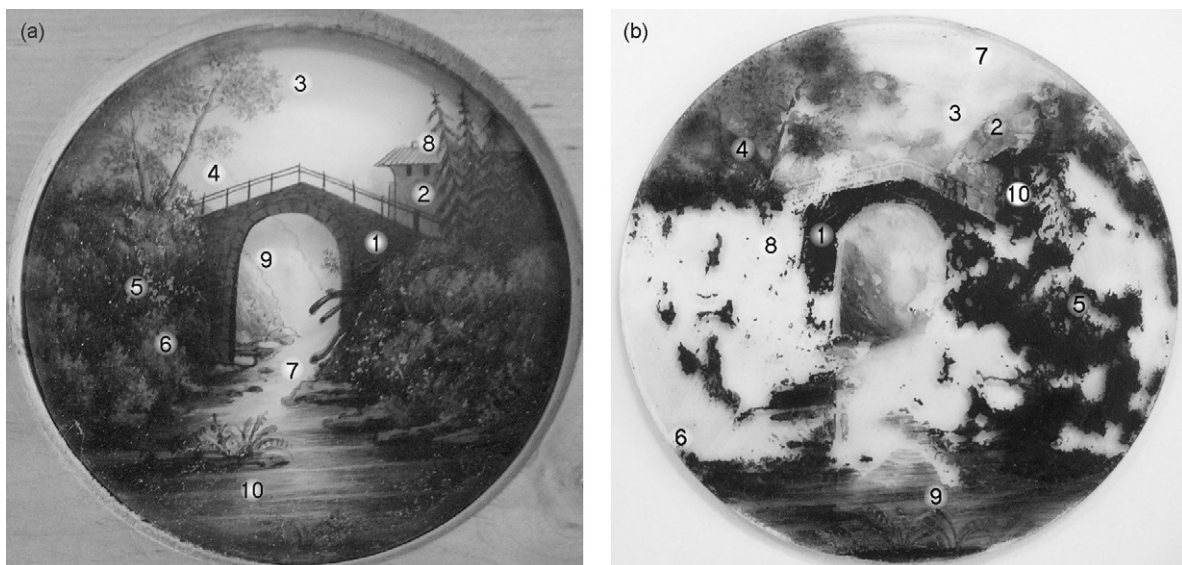


Fig. 4. The sample points on the *Ponte del Diavolo-Giorno* (a) and *Ponte del Diavolo-Notte* (b).

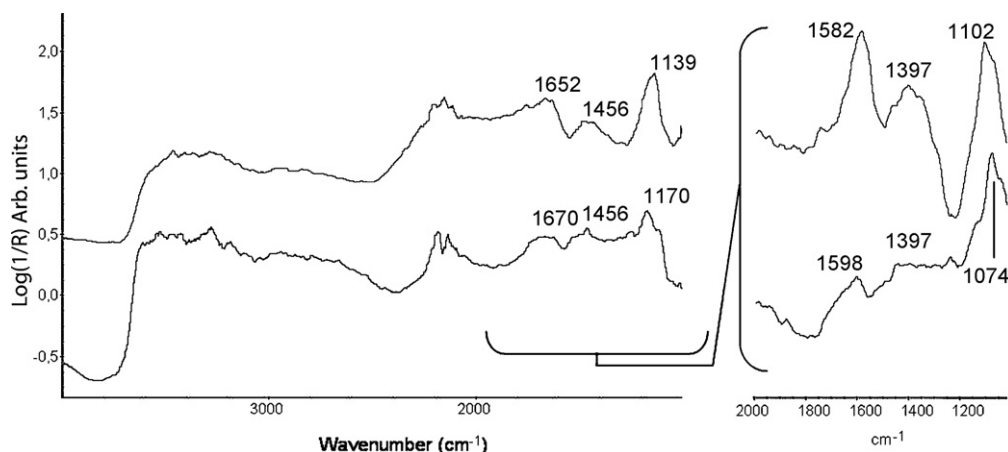


Fig. 5. Sample point 8, a pinkish part of the sky on *Ponte del Diavolo-Giorno* compared to the gum arabic reference. To the right, is the Kramers–Kronig corrected fingerprint region of the two spectra.

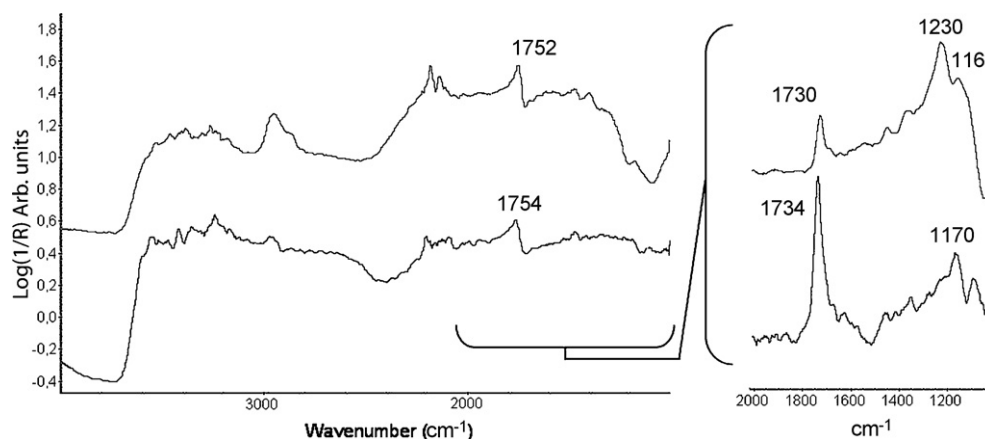


Fig. 6. Sample point 10, blue water on *Ponte del Diavolo-Giorno*, compared to the linseed oil reference. To the right, is the Kramers–Kronig corrected fingerprint region of the two spectra.

Fig. 5 shows the spectrum of point 8, a pinkish part of the sky above the roof, taken on the *Ponte del Diavolo-Giorno* with the gum arabic reference sample. This spectrum corresponded well with the gum reference with overlapping peaks at approximately

1652 cm^{-1} , 1456 cm^{-1} and 1139 cm^{-1} . The Kramers–Kronig corrected absorbances show a better correspondence between the two spectra. Fig. 6 shows the spectrum of point 10, blue water, sampled on the same magic lantern plate with the oil

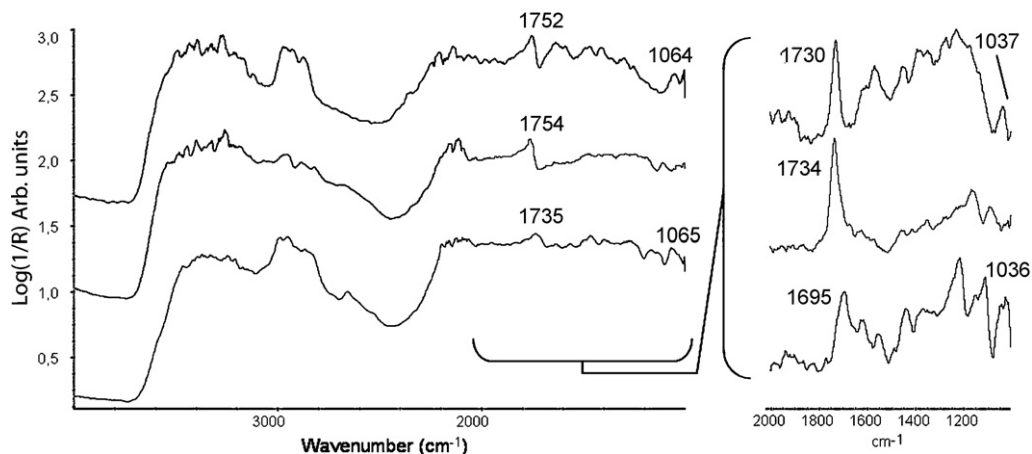


Fig. 7. Sample point 2, a brown part of the building on *Ponte del Diavolo-Giorno*, compared to the linseed oil and Venetian turpentine references. To the right, is the Kramers–Kronig corrected fingerprint region of the three spectra.

Table 1
Binders identified with mid-infrared (IR) fibre-optic reflectance spectroscopy (FORS) at the various points (as indicated in Figs. 4a and b) for the two glass magic lantern plates studied.

	Sample points	1	2	3	4	5	6	7	8	9	10
<i>Ponte del Diavolo-Giorno</i>	Gum			✓	◇	◇		^a	✓	◇	◇
	Oil	✓ ^a	✓		✓	◇	✓	✓		✓	✓
	Resin		✓ ^a			◇	^a				
<i>Ponte del Diavolo-Notte</i>	Gum	◇		✓	^a						◇
	Oil	◇	✓		✓	◇	◇	✓	✓	✓	◇
	Resin				✓	◇	◇	^a	^a	^a	

✓: present; ◇: likely present, but noise in spectra masks several peaks.

^a Possibly present in small amount.

reference sample for comparison. It can be seen that the first order derivative specular distorted carbonyl peak of the oil at 1754 cm^{-1} corresponds well to the peak found in the sample at 1752 cm^{-1} . Once again, the Kramers–Kronig correction helped in the identification of the oil binder by correcting the main peak at 1730 cm^{-1} and the peaks around 1161 cm^{-1} to 1230 cm^{-1} . A reststrahlen band may also be present at the lower limits of the spectrum of point 10; unfortunately, the end of the distortion is below the detection limits of the instrument. Finally, the spectrum of point 2 (Fig. 7), the brown area on the building, clearly shows a specular distorted C=O peak at 1752 cm^{-1} which may be assigned to an oil, as well as, additional peaks around 1465 cm^{-1} , 1300 cm^{-1} and 1052 cm^{-1} , which likely are evidence of a resin, the specific one unknown; however, all these peaks correspond well with the turpentine reference. The carbonyl peak in the resin around 1727 cm^{-1} is not observed, either because of the first order derivative specular distortion of the carbonyl peak of the oil or because the carbonyl peak of the aged resin has shifted to a higher wave number [8], closer to the carbonyl absorption of the oil. The Kramers–Kronig correction helped reveal a peak at the lower end of the spectrum around 1037 cm^{-1} which was attributed to the resin. The presence of a resin material corresponds with the literature which states that a varnish layer was often painted over the dried coloured paint layers [4]. The same results of mixed media over the magic lantern plate were observed for the *Ponte del Diavolo-Notte*. Table 1 shows the binders that have been identified for each point on both glass magic lantern plates. A summary of the main peaks observed in the mid-IR FORS and Kramers–Kronig corrected regions of the mid-IR FORS spectra of points 2, 8 and 10, as well as the reference materials in Table 2; in the case of the reference materials, the absorbance peaks in ATR are also reported for comparison purposes. The assigned peaks do not correspond exactly to each other, because of the noise in the spectra and the smoothing procedure.

These results correspond well with the results from previous FTIR-ATR studies of the binding materials on these painted glass plates [9]. To perform the ATR studies, the plates were gently placed over the ATR window and lightly pressed down to ensure minimal contact. This technique is non-destructive; however, used in this fashion, with such delicate objects, it is invasive to small extent and, above all, if too much pressure is

Table 2
Attenuated total reflectance (ATR), fibre-optic reflectance spectroscopy (FORS) and corrected FORS peak comparison of the three sample points examined in detail and the reference materials.

Samples	ATR (cm^{-1})	FORS (cm^{-1})	Kramers–Kronig (cm^{-1})
<i>References</i>			
Gum arabic			
O–H ^a	1620	1670	1602
C–H ^b	1360	1456	1343
C–O ^b	1024	1170	1074
Rabbit skin glue			
C=O ^b	1632	1704 ^c	1659
C–N–H ^a	1539	1578 ^c	1552
C–H ^a	1450	–	1454
Venetian turpentine			
C=O ^b	1695	1735 ^c	1695
C–H ^a	1446	1465	1439
C–O ^b	1038	1065 ^c	1018 ^d
Linseed oil			
C=O ^b	1742	1754 ^c	1735
C–H ^a	1459	1478	1456
C–O ^b	1161	1187	1167
<i>Sample points</i>			
Point 2 – oil/resin			
C=O ^{b,f}		1752 ^c	1732
C–H ^{a,e,f}		1465	1452
C–O ^{b,e}		1052	1037
Point 8 – gum			
O–H ^a		1652	1586
C–H ^b		1456	1380
C–O ^b		1143	1087
Point 10 – oil			
C=O ^b		1754 ^c	1732
C–H ^a		1307	1456
C–O ^b		1183	1163

^a Bending band.

^b Stretching band.

^c Distorted peak (values of upper cusp).

^d Bumpy peak, average value reported.

^e Turpentine (evidence of resin).

^f Oil (evidence of oil).

applied or if the plates are not placed correctly, it runs a high risk of being destructive as well.

4. Conclusions

Although mid-IR FORS has some limitations, it has been successfully used to non-invasively characterise the binding media used in the creation of painted glass magic lantern plates. Being delicate and fragile artefacts, a non-invasive technique such as mid-IR FORS was ideal for the analysis of the binding materials. In general, reference samples or knowledge of the sample is extremely helpful; thus, four references based on the literature were prepared on glass plates and analysed. The Kramers–Kronig correction was used to help interpret the fingerprint regions of the spectra collected, correcting several peaks, which were distorted because of specular reflection. Oil and watercolour binding materials were identified, as well as a resin material. This suggests that an oil/resin painting medium or an oil medium with a resin varnish layer were used, as well as a gum preparation layer, or painting medium, in the decoration of the glass plates. The presence of all these materials corresponded to document painting methods of glass plates for magic lanterns.

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